SPECIFICATION

Title of the Invention

IMPURITY DOPING METHOD FOR SEMICONDUCTOR AS WELL AS SYSTEM
THEREFOR AND SEMICONDUCTOR MATERIALS PREPARED THEREBY

Background of the Invention

Field of The Invention

The present invention relates to an impurity doping method
for semiconductor as well as to a system therefor and semiconductor
materials prepared thereby, and more particularly to an impurity
doping method for semiconductor used suitably in case of preparing
a semiconductor material having a high conductance as well as
a system therefor and semiconductor materials each having a high
conductance prepared thereby.

Description of The Related Art

Heretofore, there has been known an impurity doping method
for semiconductor wherein plural types of crystal raw materials
and plural types of impurity raw materials are used in a
predetermined crystal growth device or the like in case of
preparing a semiconductor material, and both of the crystal raw
materials and the impurity raw materials are continuously supplied,
whereby a crystal layer formed on a substrate from the crystal
raw materials is doped with the impurities.

Meanwhile, in such conventional impurity doping method for
semiconductor as described above, since both these plural types
of crystal raw materials and these plural types of impurity raw

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materials are continuously supplied, plural types of impurities are disorderly incorporated into an atomic layer of crystals to be formed on a substrate from the crystal raw materials.

For this reason, when these plural types of impurity raw materials involve p-type impurity raw materials and n-type impurity raw materials, respectively, the p-type impurity raw materials and the n-type impurity raw materials cancel with each other (compensation effect), so that a carrier concentration becomes a difference defined between concentrations of these p- and n-type impurity raw materials. Accordingly, there has been such a problem that a carrier concentration of a semiconductor material to be fabricated decreases, and it results in a low conductance.

Furthermore, when both of plural types of crystal raw materials and plural types of impurity raw materials are continuously supplied to prepare a p-type semiconductor material in accordance with a conventional impurity doping method for semiconductor, an impurity level in a forbidden gap of the p-type semiconductor material is deep; and the p-type semiconductor exhibits high activation energy. Accordingly, there has been also such a problem that positive hole having a high density cannot be obtained, and it results in a low conductance.

Object and Summary of The Invention

The present invention has been made in view of the above-described problems involved in the prior art, and an object of the invention is to provide an impurity doping method for semiconductor by which a carrier concentration is adapted to

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increase, whereby a semiconductor material having a high conductance can be prepared, even in the case when a crystal layer is doped with p-type impurity raw materials and n-type impurity raw materials as well as to provide a system for preparing such semiconductor materials.

Furthermore, another object of the present invention is to provide an impurity doping method for semiconductor and a system therefor by which a p-type semiconductor material with positive hole having a high density and exhibiting a high conductance can be prepared.

Moreover, a further object of the present invention is to provide a semiconductor material having a high conductance.

In order to achieve the above-described objects, an impurity doping method for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities according to the present invention comprises each of plural types of impurity raw materials being supplied at close timings in a pulsed manner within one cycle wherein all types of the crystal raw materials are supplied in one time each in the case when plural types of the crystal raw materials are alternately supplied in a pulsed manner with maintaining each of predetermined purge times.

Furthermore, an impurity doping method for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities according to the present invention comprises each of plural types of impurity raw materials being supplied at close timings in a pulsed manner either at the same time of, or after starting a supply of predetermined types of crystal raw materials as well as before starting a supply of the other predetermined

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types of crystal raw materials within one cycle wherein all types of the plural types of crystal raw materials are supplied in one time each in the case when plural types of the crystal raw materials are alternately supplied in a pulsed manner with maintaining each of predetermined purge times.

Moreover, an impurity doping method for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities according to the present invention comprises a first impurity raw material and a second impurity material being supplied at close timings in a pulsed manner either at the same time of, or after starting a supply of the first crystal raw material as well as before starting a supply of the second crystal raw material within one cycle wherein the first and second crystal raw materials are supplied in one time each in the case when the first crystal raw material is supplied alternately with the second crystal raw material in a pulsed manner with maintaining each of predetermined purge times.

As a result, according to the present invention, a carrier concentration comes to increase in case of doping a crystal layer with plural types of impurity raw materials, whereby a semiconductor material having a high conductance can be prepared.

In an impurity doping method for semiconductor of the present invention, it may be arranged in such that a supply of the first impurity raw material is started in synchronous with starting a supply of the first crystal raw material, a supply of the second impurity raw material is started after finishing the supply of the first impurity raw material, and the supply of the second impurity raw material is finished before starting the supply of

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the second crystal raw material.

Furthermore, in an impurity doping method for semiconductor of the present invention, it may be arranged in such that there is a period of time wherein the first impurity raw material is supplied with the second impurity raw material at the same time.

Moreover, in an impurity doping method for semiconductor of the present invention, it may be arranged in such that a crystal raw material supplied precedently within the one cycle in the crystal raw materials is at least one member selected from the group consisting of Ga, Al, In, B, Zn, and Cd, while a crystal raw material supplied latterly within the one cycle is at least one member selected from the group consisting of N, As, P, S, Se, and Te.

Still further, in an impurity doping method for semiconductor of the present invention, it may be arranged in such that the impurity raw materials are a p-type impurity raw material and an n-type impurity raw material.

Thus, according to the present invention, a p-type semiconductor material with a positive hole of a high density and having a high conductance can be prepared.

Furthermore, an impurity doping method for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities according to the present invention comprises a cycle composed of a first step wherein a supply of TMGa and $(Cp)_2Mg$ is started at a first timing, and the supply of TMGa and $(Cp)_2Mg$ is finished at a second timing at which the supply of TMGa and $(Cp)_2Mg$ for a predetermined period of time was completed; a second step wherein a supply of TESi is started either immediately after,

or after the second timing at which the supply of TMGa and $(Cp)_2Mg$ was finished, and the supply of TESi is finished at a third timing at which the supply of TESi for a predetermined period of time was completed; a third step wherein a supply of NH_3 is started either immediately after, or after the third timing at which the supply of TESi is finished, and the supply of NH_3 is finished at a fourth timing at which the supply of NH_3 for a predetermined period of time was completed; and a fourth step wherein a predetermined purge time is started after the supply of NH_3 is finished at the fourth timing at which the supply of NH_3 was completed, and the predetermined purge time is finished at a fifth timing; being repeated a desired number of times.

Thus, according to the present invention, a carrier concentration comes to increase, a semiconductor material having a high conductance can be prepared in the form of GaN, and further, a p-type semiconductor material with a positive hole of a high density and having a high conductance can be prepared in the case where a GaN crystal layer is doped with Mg and Si as impurity raw materials.

Moreover, a semiconductor material prepared by doping a crystal layer with plural types of impurities according to the present invention comprises the plural types of impurities being disposed closely with each other in the crystal layer at a predetermined ratio.

As a result, according to the present invention, a semiconductor material having a high conductance can be prepared.

Still further, a semiconductor material prepared by doping a crystal layer made of Ga with Mg and Si according to the present

invention comprises Mg and Si being disposed closely with each other in the crystal layer made of Ga at a predetermined ratio.

Hence, according to the present invention, a p-type semiconductor material with a positive hole of a high density and having a high conductance can be prepared.

Yet further, an impurity doping system for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities comprises a reaction tube to the interior of which is disposed a substrate; a plurality of pipes for supplying raw material gases of the crystal raw materials as well as for supplying raw material gases of impurity raw materials into the reaction tube, respectively; gas valves mounted on the plurality of pipes, respectively; a flow rate setting means for setting out each flow rate of the raw material gases of the crystal raw materials and the raw material gases of the impurity raw materials flowing through the plurality of pipes, respectively, to a predetermined value; a heating means for heating the substrate disposed inside the reaction tube; and a control means for controlling closing motions of the gas valves, flow rates set out by the flow rate setting means, heating of the substrate by means of the heating means, and controlling further in such that the raw material gases of the crystal raw materials and the raw material gases of the impurity raw materials are supplied into the reaction tube through the pipes at predetermined timings, respectively, in a pulsed manner.

As a result, according to the present invention, a carrier concentration comes to increase, and a semiconductor material having a high conductance can be prepared.

Further, an impurity doping system for semiconductor wherein a crystal layer made of crystal raw materials is doped with impurities according to the present invention comprises a reaction tube to the interior of which is disposed a substrate; a first pipe for supplying NH_3 gas into the reaction tube together with H_2 gas being a carrier gas; a second pipe for supplying TMGa, $(Cp)_2Mg$, and TESi into the reaction tube together with H_2 gas being a carrier gas; a third pipe for supplying N_2 gas being a carrier gas into the reaction tube; gas valves mounted on the first, second, and third pipes, respectively; a flow rate setting means for setting out each flow rate of gases flowing through the first, second, and third pipes, respectively, to a predetermined value; a heating means for heating the substrate disposed inside the reaction tube; and a control means for controlling closing motions of the gas valves, flow rates set out by the flow rate setting means, heating of the substrate by means of the heating means, and controlling further in such that NH_3 gas is supplied in the reaction tube through the first pipe, TMGa, $(Cp)_2Mg$, and TESi are supplied into the reaction tube through the second pipe, and N_2 gas is supplied into the reaction tube through the third pipe at predetermined timings, respectively, in a pulsed manner.

Thus, according to the present invention, a carrier concentration comes to increase, a semiconductor material having a high conductance can be prepared in the form of GaN, and further, a p-type semiconductor material with a positive hole of a high density and having a high conductance can be prepared in the case where a GaN crystal layer is doped with Mg and Si as impurity

raw materials.

Brief Description of The Drawing

The present invention will become more fully understood from the detailed description given hereinafter and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

FIG. 1 is a schematic constitutional explanatory view illustrating an essential part of a crystal growth system by which an impurity doping method for semiconductor according to the present invention is realized;

FIG. 2 is an explanatory diagram showing timings for supplying crystal raw materials and impurity raw materials in accordance with an impurity doping method for semiconductor of the present invention;

FIG. 3 is an explanatory view showing schematically a crystal structure of a semiconductor material formed in accordance with an impurity doping method for semiconductor of the present invention;

FIG. 4 is a schematic constitutional explanatory view showing an MOCVD system by which formation of GaN crystal is realized in accordance with an impurity doping method for semiconductor of the present invention;

FIG. 5 is a schematic constitutional explanatory view showing an essential part of the system shown in FIG. 4;

FIG. 6 is a schematic constitutional explanatory view showing the reaction tube of FIG. 4;

FIG. 7 is an explanatory diagram showing timings for

supplying crystal raw materials and impurity raw materials in the case where GaN crystal is formed in accordance with an impurity doping method for semiconductor of the present invention;

FIG. 8 is an explanatory view showing schematically a GaN crystal structure formed in accordance with an impurity doping method for semiconductor of the present invention;

FIG. 9 is a graphical representation showing positive hole concentrations of a p-type GaN prepared in accordance with an impurity doping method for semiconductor of the present invention without supplying TESi; and

FIG. 10 is a graphical representation showing positive hole concentrations of a p-type GaN prepared in accordance with an impurity doping method for semiconductor of the present invention.

Detailed Description of The Preferred Embodiments

In the following, embodiments of an impurity doping method for semiconductor as well as a system therefor and semiconductor materials prepared thereby will be described in detail by referring to the accompanying drawings.

FIG. 1 is a schematic constitutional explanatory view illustrating an essential part of a crystal growth system by which an impurity doping method for semiconductor according to the present invention is realized; FIG. 2 is an explanatory diagram showing timings for supplying crystal raw materials and impurity raw materials in accordance with an impurity doping method for semiconductor of the present invention; and FIG. 3 is an explanatory view showing schematically a crystal structure of a semiconductor material formed in accordance with an impurity

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doping method for semiconductor of the present invention.

In order to achieve easy understanding of the present invention, an outline of an impurity doping method for semiconductor according to the present invention will be described herein. Into a reaction tube (made of, for example, quartz glass) of a crystal growth system inside of which a substrate has been placed, crystal raw materials and impurity raw materials are supplied respectively in a pulsed manner at each of predetermined timings through pipes (each made of, for example, quartz glass) and the like, so that the crystal raw materials and the impurity raw materials thus supplied react with each other in the reaction tube, whereby a crystal structure is formed on the substrate (see FIG. 1).

Specifically, according to an impurity doping method for semiconductor of the present invention wherein crystal formation is made by the use of a crystal raw material A, a crystal raw material B, a p-type impurity raw material C, and an n-type impurity raw material D (see FIG. 2), all of the crystal raw material A, the crystal raw material B, the p-type impurity raw material C, and the n-type impurity raw material D are not continuously supplied, but supplied for only a predetermined period of time, in other words, supply of these raw materials is stopped for the period of time other than the predetermined time, that is, these raw materials are supplied in a pulsed manner.

Furthermore, the crystal raw material A is alternately supplied with a predetermined purge time T_{pa} with respect to the crystal raw material B with a predetermined purge time T_{pb} in a pulsed manner. As a result, the crystal raw material A is not

supplied at the same timing as that of the crystal raw material B.

On the other hand, the p-type impurity raw material C and the n-type impurity raw material D are supplied either synchronously with the crystal raw material A, or they are supplied after commencement of supplying the crystal raw material A and before commencement of supplying the crystal raw material B in a pulsed manner, besides, the p-type impurity raw material C is supplied with the n-type impurity raw material D at a close timing.

More specifically, the crystal raw material A is started to be supplied, for example, together with the p-type impurity raw material C at timing T1.

Then, the crystal raw material A is supplied at a predetermined time t_A, and further the p-type impurity raw material C is supplied for a predetermined time t_C being equal to the predetermined time t_A, and supply of the crystal raw material A and the p-type impurity raw material C is completed at a timing T2.

Thereafter, immediately after the timing T2 at which supply of the p-type impurity raw material C is completed, supply of the n-type impurity raw material D is started and continued for a predetermined time t_D, and the supply of the n-type impurity raw material D is completed at timing T3.

Furthermore, supply of the crystal raw material B is commenced immediately after the timing T3 and continued for a predetermined time t_B, and the supply thereof is finished at timing T4.

After completing the supply of the crystal raw material B,

a predetermined purge time T_{pb} is taken, and the purge time T_{pb} is finished at timing T5.

Processing of one cycle is completed as described above, and the following cycle is started again wherein the timing T5 is deemed to be a timing T1.

When such cycle as described above is repeated by a desired number of times, crystal having a desired film thickness can be obtained as a semiconductor material.

More specifically, as described above, when a unit of operation wherein one each supply of all the crystal raw material A, the crystal raw material B, the p-type impurity raw material C, and the n-type impurity raw material D is conducted, in other words, when one cycle extending from the timing T1 to the timing T5 is repeated, crystal having a desired thickness is formed.

A timing for supplying the n-type impurity raw material D is not limited to that being immediately after the timing T2 at which a supply of the p-type impurity raw material C was finished, but it may be the timing T1 at which a supply of the p-type impurity raw material C was started.

Namely, a time T_{cd} defined between a timing for starting supply of the p-type impurity raw material C (see the timing T1 in FIG. 2) and a timing for starting supply of the n-type impurity raw material D (see the timing T2 in FIG. 2) may be from zero or longer to a predetermined time t_c or shorter wherein there may be a period in which the p-type impurity raw material C is supplied together with the n-type impurity raw material D.

Furthermore, a timing for supplying the p-type impurity raw material C is not limited to that synchronizing with the timing

T1 at which a supply of the crystal raw material A was started, but it may be later than the timing T1 at which the crystal raw material A was started.

In brief, the p-type impurity raw material C and the n-type impurity raw material D are supplied at either the same time of starting a supply of the crystal raw material A, or a close timing after the supply thereof and before starting a supply of the crystal raw material B.

A crystal structure formed in accordance with the timings shown in FIG. 2 involves a layer 102 composed of the crystal raw material A formed on a substrate 100 as a result of supplying the crystal raw material A for a predetermined time t_A from the timing T1 as shown in FIG. 3.

It is considered in this case that a kind of an impurity pair composed of the p-type impurity raw material C and the n-type impurity raw material D has been formed in the layer 102 made of the crystal raw material A as a result of supplying the p-type impurity raw material C and the n-type impurity raw material D.

Then, a layer 104 made of the crystal raw material B is laminated on the layer 102 made of the crystal raw material A as a result of supplying the crystal raw material B for a predetermined time t_B from a timing T3.

Furthermore, when a desired number of times of the above-described one cycle (see FIG. 2) is repeated, lamination of the layer 102 made of the crystal raw material A and the layer 104 made of the crystal raw material B is repeated in response to the number of times of cycle repeated, whereby crystal having a desired thickness W is formed, and thus, the resulting crystal

can be used for a semiconductor material.

As described above, it is considered that a kind of an impurity pair is formed from the p-type impurity raw material C and the n-type impurity raw material D in the layer 102 made of the crystal raw material A.

In the following, a case where a layer of GaN crystal as a semiconductor material is formed on a substrate in accordance with an impurity doping method for semiconductor of the present invention will be described by referring to FIG. 4 through 8.

FIG. 4 is a schematic constitutional explanatory view showing a Metalorganic Chemical Vapor Deposition (MOCVD) system by which GaN crystal is formed as a semiconductor material in accordance with an impurity doping method for semiconductor of the present invention.

Further, FIG. 5 is a schematic constitutional explanatory view showing an essential part of the system shown in FIG. 4, FIG. 6 is a schematic constitutional explanatory view showing the reaction tube shown in FIG. 4, FIG. 7 is an explanatory diagram showing timings for supplying crystal raw materials and impurity raw materials in the case where GaN crystal is formed in accordance with an impurity doping method for semiconductor of the present invention, and FIG. 8 is an explanatory view showing schematically a GaN crystal structure formed in accordance with an impurity doping method for semiconductor of the present invention.

In the following description, trimethylgallium (TMGa) is used for a raw material gas of gallium (Ga) being a crystal raw material as well as ammonia (NH_3) is used for a raw material gas of nitrogen (N) being a crystal raw material in case of subjecting

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GaN to crystal growth.

Moreover, biscyclopentadienyl magnesium ($(Cp)_2Mg$) is used for a raw material gas of magnesium (Mg) being an impurity material (p-type impurity raw material) for doping use, while tetraethylsilane (TESi) is used for a raw material gas of silicon (Si) being an impurity material (n-type impurity raw material) for doping use.

First, an outline of an MOCVD system 10 shown in FIG. 4 is explained. The MOCVD system 10 comprises a reaction tube 12 the inside of which is provided with a substrate 200, a bubbler 14 for retaining trimethylgallium (TMGa), NH_3 bombs 16-1 and 16-2 each for retaining ammonia (NH_3) gas, a bubbler 18 for retaining biscyclopentadienyl magnesium ($(Cp)_2Mg$), a bubbler 20 for retaining tetraethylsilane (TESi), an H_2 bomb 22 for retaining hydrogen (H_2) gas being a carrier gas, an N_2 bomb 24 for retaining nitrogen (N_2) gas being a carrier gas, a controller 26 for effecting a variety of controls (for example, a control for closing motions of the undermentioned various gas valves and pressure regulators, a control for the undermentioned various mass flow controllers for the sake of setting a flow rate in a variety of gases introduced into the reaction tube 12 to a predetermined value, a control for temperature of the substrate 200 based on a control for energization of high-frequency current upon the undermentioned high-frequency coil 32 for heating substrate, and the like controls), a rotary pump 28 used as an exhauster for implementing exhaust inside the reaction tube, and an exhaust gas processor 30 for processing exhaust from the rotary pump 28.

In the above-described constitution, the high-frequency

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coil 32 for heating substrate is wound around the outer circumferential region of the reaction tube 12. Inside the reaction tube 12, a carbon susceptor 34 for supporting the substrate 200 is disposed, and a thermocouple 36 to be mounted to the carbon susceptor 34 is disposed.

Namely, high-frequency current is energized upon the high-frequency coil 32 for heating substrate to heat the carbon susceptor 34, whereby the substrate 200 mounted on the carbon susceptor 34 is heated to a predetermined temperature in the MOCVD system 10.

A temperature of the carbon susceptor 34 is monitored by the thermocouple 36, and a high-frequency current energized to the high-frequency coil 32 for heating substrate is controlled by means of the controller 26 based on results of the monitoring, whereby a temperature of the substrate 200 is controlled in such a manner that the substrate 200 is heated to a predetermined temperature.

Moreover, a quartz pipe 40 for supplying NH_3 gas from the NH_3 bombs 16-1 and 16-2 into the reaction tube 12, a quartz pipe 42 for supplying H_2 gas as a carrier gas from the H_2 bomb 22, and a quartz pipe 43 for supplying N_2 gas as a carrier gas from the N_2 bomb 24 are disposed in the reaction tube 12, respectively.

The NH_3 gas retained in the NH_3 bombs 16-1 and 16-2 is adapted in such that when gas valves 57, 59, 60, and 61 are opened respectively, it is supplied into the reaction tube 12 together with H_2 gas at a gas flow rate which has been set to each predetermined value by means of mass flow controllers (MFCs) 50 and 51 through the quartz pipe 40.

Furthermore, the H_2 gas retained in the H_2 bomb 22 is adapted in such that when gas valves 67, 68, and 69 are opened, it is delivered from a hydrogen purifier 70 through a gas valve 80 and a pressure reducing valve 81 to the bubblers 14, 18, and 20 at a gas flow rate which has been set to each predetermined value by means of MFCs 54, 55, and 56.

In this case, the bubbler 14 is provided with a thermostatic chamber 72, the bubbler 18 is provided with a thermostatic chamber 74, and the bubbler 20 is provided with a thermostatic chamber 76, respectively. When the gas valves 64, 65, and 66 are opened together with the gas valve 62, the TMGa, the $(Cp)_2Mg$, and the TESi retained in the bubblers 14, 18, and 20 and maintained at a predetermined temperature, respectively, are supplied together with an H_2 carrier gas at a gas flow rate which has been set to a predetermined value by means of the MFC 52 into the reaction tube 12 through the quartz pipe 42, respectively.

On one hand, the N_2 gas retained in the N_2 bomb 24 is adapted in such that when the gas valve 63 is opened, it is supplied into the reaction tube 12 at a gas flow rate which has been set to a predetermined value by means of the MFC 53 through the quartz pipe 43.

Controls for gas flow rates by means of the MFCs 50, 51, 52, 53, 54, 55, and 56 as well as controls for closing motions of the gas valves 57, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, and 80 as well as for closing motions of the pressure reducing valve 81 are made by means of the controller 26.

In the above-described constitution, first, a pressure in the reaction tube 12 is reduced to 76 Torr (0.1 atmospheric

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pressure), and a temperature of the substrate 200 (SiC (silicon carbide) substrate is used for the substrate 200) mounted on the carbon susceptor 34 is heated to 950°C in the MOCVD system 10 for forming GaN crystal as a semiconductor material in accordance with an impurity doping method for semiconductor of the present invention.

Furthermore, the controller 26 controls the MFCs 50, 51, 52, and 53, whereby a flow rate of NH_3 gas is controlled to one liter/minute, a flow rate of H_2 gas is controlled to two to five liter/minute, and a flow rate of N_2 gas is controlled to one to three liter/minute, respectively.

Namely, it is preferred that an internal pressure in the reaction tube 12 is reduced to 0.1 atmospheric pressure, and each flow rate of various raw material gases is made to be several meters/second in order to keep each switching time of the various raw material gases (TMGa gas for supplying Ga as a crystal raw material, NH_3 gas for supplying N as a crystal raw material, $(CP)_2Mg$ gas for supplying Mg as a p-type impurity raw material, and TESi gas for supplying Si as an n-type impurity raw material) one-tenth second or faster on the SiC substrate 200 in the reaction tube 12.

It is to be noted that an AlGaN buffer layer 201 (see FIG. 8) has been previously formed with a thickness of 300 nm at 1150°C on the SiC substrate 200 mounted on the carbon susceptor 34 in accordance with a well-known technique.

As shown in FIG. 7, TMGa and NH_3 are alternately supplied for one second each to form GaN crystal while maintaining each of one-second purge times T_{pa} and T_{pb}. In this case, $(Cp)_2Mg$ of

a p-type impurity raw material is supplied for the same period of time as that of the TMGa, while TESi of an n-type impurity raw material is supplied for one second after supplying the $(Cp)_2Mg$, i.e., during only the purge time T_{pa}.

In order to prevent such a phenomenon that nitrogen atom is vaporized again from the GaN crystal formed during stopping a supply of NH_3 under a high temperature, resulting in deterioration of quality in the crystal formed, a low flow rate (50 cc) of NH_3 is continuously supplied.

More specifically, a supply of TMGa and $(Cp)_2Mg$ is first started at a timing T1.

The TMGa is supplied for one second (a predetermined time t_A) as well as the $(Cp)_2Mg$ is supplied for one second (a predetermined time t_C) equal to a predetermined time t_A, and the supply of the TMGa and the $(Cp)_2Mg$ is finished at a timing T2.

Thereafter, a supply of TESi is started immediately after the timing T2 at which supply of $(Cp)_2Mg$ is finished, the TESi is supplied for one second (a predetermined time t_D), and the supply of TESi is finished at a timing T3.

Furthermore, a supply of NH_3 is started immediately after the timing T3, the NH_3 is supplied for one second (a predetermined time t_B), and the supply of NH_3 is finished at timing T4.

After finishing the supply of NH_3, a predetermined purge time T_{pb} (one second) is executed, and the purge time T_{pb} is finished at timing T5.

Processing of one cycle is completed in accordance with the above-described manner, and the following cycle is started from the timing T5 as timing T1.

When such cycle as described above is repeated by a desired number of times, GaN crystal having a desired film thickness can be obtained as a semiconductor material.

In a structure of GaN crystal formed in accordance with the timings shown in FIG. 7, a layer 202 made of Ga is formed on the AlGaN buffer layer 201 prepared on the SiC substrate 200 by means of a supply of TMGa for one second (a predetermined time t_A) from a timing T1 as shown in FIG. 8.

In this case, a kind of impurity pair (Mg-Si) made from Mg being a p-type impurity raw material and Si being an n-type impurity raw material is formed in a layer 202 made of Ga as a result of supplying Mg of $(Cp)_2Mg$ being a p-type impurity raw material and Si of TESi being an n-type impurity raw material.

Then, a layer 204 made of N is laminated on the layer 202 made of Ga as a result of supplying NH_3 in case of starting from the timing T3 (a predetermined time t_B).

One cycle wherein TMGa, NH_3, $(Cp)_2Mg$ and TESi are supplied (see FIG. 7) in accordance with a manner as described above corresponds to four seconds, so that when a desired number of times for this one cycle is repeated, lamination of the layer 202 made of Ga and the layer 204 made of N is repeated in response to a repeated number of times for the cycle, GaN crystal having a desired thickness W is formed, whereby the GaN crystal prepared may be used as a semiconductor.

More specifically, when a raw material gas $(Cp)_2Mg$ of Mg being a p-type impurity raw material and a raw material gas TESi of Si being an n-type impurity raw material are supplied in a pulsed manner at a close timing either at the same time of starting

a supply of a raw material gas TMGa of Ga being a crystal raw material gas, or after the supply thereof and before starting a supply of a raw material gas NH_3 of N being a crystal raw material as described above, the layer 202 made of Ga is doped with Mg and Si at an appropriate ratio without incorporating disorderly Mg and Si into the layer.

Thus, positions of Mg and Si in the layer 202 made of Ga are controlled, whereby Mg and Si are placed at a close relationship with each other at a predetermined ratio in the layer 202 made of Ga, so that Mg forms a kind of impurity pair with Si, and it results in decrease of energy level, i.e., decrease of activation energy.

Accordingly, a carrier concentration increases in GaN crystal, whereby a semiconductor material having a high conductance can be obtained.

Furthermore, FIGS. 9 and 10 indicate experimental results made by the present applicant in accordance with a constitution of the system as well as conditions therefor shown in FIGS. 4 through 7.

The experimental results of FIGS. 9 and 10 are represented by graphs each indicating positive hole concentrations of p-type GaN prepared in accordance with an impurity doping method for semiconductor of the present invention. It is to be noted that the p-type GaN used in the experiment shown in FIG. 9 is the ones each having a crystal structure prepared in accordance with the above-described timings shown in FIG. 7, but no raw material gas TESi of Si being an n-type impurity raw material has not been supplied (for a predetermined time t_D), and it has been prepared

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by changing only a supply flow rate of a raw material gas $(Cp)_2Mg$ of Mg being a p-type impurity raw material.

As shown in FIG. 9, when GaN crystal is prepared as a semiconductor material by supplying only one impurity raw material (Mg) without using plural types of impurity raw materials in accordance with an impurity doping method for semiconductor of the present invention, a carrier concentration of p-type GaN is 2.6×10^{18} cm^{-3} in case of 9 sccm supply flow rate of $(Cp)_2Mg$, while a carrier concentration of p-type GaN is 5.4×10^{18} cm^{-3} in case of 20 sccm supply flow rate of $(Cp)_2Mg$.

Accordingly, it is found that a carrier concentration of p-type GaN increases in proportion to a supply flow rate of $(Cp)_2Mg$ within a range of from 9 sccm to 20 sccm of a raw material gas $(Cp)_2Mg$ of Mg being a p-type impurity raw material.

In the following, an explanation will be made by referring to the experimental results shown in FIG. 10, these results are represented by a graph indicating concentrations of positive hole of p-type GaN prepared in accordance with an impurity doping method for semiconductor of the present invention. It is to be noted that the p-type GaN shown in FIG. 10 has a crystal structure prepared in accordance with the above-described timings shown in FIG. 7 wherein raw material gas $(Cp)_2Mg$ of Mg being a p-type impurity raw material is supplied constantly at 9 sccm and at the same time, a supply flow rate of raw material gas TESi of Si being an n-type impurity raw material is changed.

As shown in FIG. 10, when a semiconductor material is prepared by supplying plural types of impurity raw materials (Mg and Si) in accordance with an impurity doping method for semiconductor

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of the present invention, a carrier concentration of p-type GaN is 1.9×10^{18} cm^{-3} in case of 0.15 sccm supply flow rate of TESi, while a carrier concentration of p-type GaN is 1.1×10^{19} cm^{-3} in case of 0.25 sccm supply flow rate of TESi.

Accordingly, when TESi is not supplied in the case where a supply flow rate of $(Cp)_2Mg$ is 9 sccm (see FIG. 9), a carrier concentration of p-type GaN is 2.6×10^{18} cm^{-3}, while when TESi is supplied at 0.25 sccm (see FIG. 10), a carrier concentration of p-type GaN is 1.1×10^{19} cm^{-3}, so that a carrier concentration of the p-type GaN becomes about four times higher.

As described above, an impurity doping method for semiconductor according to the present invention comprises each of plural types of impurity raw materials being supplied at close timings in a pulsed manner either at the same time of, or after starting a supply of either types of crystal raw materials as well as before starting a supply of the other types of crystal raw materials in the case when the plural types of the crystal raw materials are alternately supplied in a pulsed manner with maintaining each of predetermined purge times T_{pa} and T_{pb}. Accordingly, a crystal layer is doped with the plural types of impurities at a proper ratio without incorporating disorderly the plural types of impurities into an atomic layer of a crystal formed on a substrate from the crystal raw materials, whereby a carrier concentration is increased in even the case where p-type impurity raw materials and n-type impurity raw materials are used, so that it becomes possible to prepare a semiconductor material having a high conductance.

Furthermore, according to an impurity doping method for

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semiconductor of the present invention, since decrease in activation energy is intended in even a p-type semiconductor material an impurity level of which in forbidden gap is deep and having high activation energy, such a semiconductor material with positive hole of a high density and having a high conductance can be prepared.

Moreover, according to an impurity doping method for semiconductor of the present invention, since it has been constituted in such that plural types of impurities are supplied at close timings in a pulsed manner, but not supplied continuously, an amount of each impurity raw material to be incorporated into an atomic layer of crystal formed on a substrate from crystal raw materials can be controlled, so that it becomes possible to prepare a semiconductor material wherein the interior of the atomic layer in the crystal is doped with impurities at each proper ratio, whereby a carrier concentration thereof is increased.

For this reason, such a theoretical concept that two types of impurities are supplied at each proper ratio, whereby an impurity level is changed to result in increase of a ratio of activation can be realized by an impurity doping method for semiconductor according to the present invention.

Still further, since a semiconductor material having a high conductance, particularly a p-type semiconductor material with positive hole of a high density and having a high conductance can be prepared by an impurity doping method for semiconductor according to the present invention as described above, it becomes possible to realize p-n junction of a high efficiency, so that it can contribute to elevation of semiconductor device

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characteristics such as increase in injection efficiency of p-n junction, decrease in contact resistance, and decrease in series resistance.

The above-described embodiments may be modified as in the manners explained in the following paragraphs (1) through (4).

(1) Although each of the above-described embodiments has been described in the case where GaN crystal is prepared, the invention is not limited thereto as a matter of course, a semiconductor material may be prepared from a variety of crystals such as AlGaN crystal, and InGaN crystal by employing either the above-described MOCVD system 10, or the other crystal growth apparatuses in accordance with an impurity doping method for semiconductor of the present invention.

In this case, a variety of conditions may be changed. For instance, when it is intended to prepare AlGaN crystal, TMAl may have been retained in the bubbler 14 in place of TMGa, while TMIn may have been retained in the bubbler 14 in the case where formation of InGaN crystal is intended.

(2) Although Ga and B have been used as each of crystal raw materials A and B as well as Mg and Si have been used as each of impurity raw materials C and D, respectively, in those of FIGS. 1 through 3 in each of the above-described embodiments, the invention is not limited thereto, as a matter of course.

For instance, the groups III and II elements such as Al, In, B, Zn, and Cd may be used other than Ga as a crystal raw material A, the groups V and VI elements such as As, P, S, Se, and Te may be used other than N as a crystal raw material B, Be may be used other than Mg as an impurity raw material C, and O may be used

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other than Si as an impurity raw material D.

Furthermore, not only a single type of material, but also two or more types of materials may be used with respect to the crystal raw materials A and B, respectively. For instance, when a mixed crystal composed of crystal raw materials A and A' as well as crystal raw materials B and B' is formed also, a semiconductor material may be prepared by adding required changes to an impurity doping method for semiconductor according to the present invention.

(3) Although it has been arranged in each of the above-described embodiments in such that a supply of an n-type impurity raw material D (TESi) is started immediately after a timing T2 at which a supply of a p-type impurity raw material C ((Cp)$_2$Mg) is finished, the invention is not limited thereto as a matter of course, but it may be arranged in such that a supply of the n-type impurity raw material D (TESi) is started after finishing a supply of the p-type impurity raw material C ((Cp)$_2$Mg) through a predetermined purge time.

While it has been arranged in each of the above-described embodiments in such that a supply of crystal raw material B (NH$_3$) is started immediately after a timing T3 at which a supply of an n-type impurity raw material D (TESi) is finished, the invention is not limited thereto as a matter of course, but it may be arranged in such that a supply of the crystal raw material D (NH$_3$) is started after finishing a supply of the n-type impurity raw material D (TESi) through a predetermined purge time.

(4) Each of the above-described embodiments may properly be combined with the above-described modified examples (1) through

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(3), respectively.

Since the present invention has been constituted as described above, such an excellent advantage that a semiconductor material having a high conductance can be prepared as a result of increasing a carrier concentration even in the case where a crystal layer is doped with p-type impurity raw materials and n-type impurity raw materials.

Moreover, there is such an excellent advantage that a p-type semiconductor material with positive hole of a high density and having a high conductance can be prepared.

It will be appreciated by those of ordinary skill in the art that the present invention can be embodied in other specific forms without departing from the spirit or essential characteristics thereof.

The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive. The scope of the invention is indicated by the appended claims rather than the foregoing description, and all changes that come within the meaning and range of equivalents thereof are intended to be embraced therein.

The entire disclosure of Japanese Patent Application No. 2000-264743 filed on September 1, 2000 including specification, claims, drawing and summary are incorporated herein by reference in its entirety.